

VARLAMOV, A.I.; GOLUBEV, A.V.; AKHOBADZE, A.V. (Gruzinskaya SSR)

Production and use of peat fertilizers and litter. Torf. prom.  
37 no.5:21-22 '60. (MIRA 14:10)

1. Moskovskiy oblastnoy sovnarkhoz (for Varlamov). 2.  
Smolenskiy oblispolkom (for Golubev).  
(Peat)  
(Fertilizers and manures)

GOGORISHVILI, P.V.; CHKONIYA, T.V.; AKHOBADZE, D.A.

Diaminosulfate and diaminosulfite complex compounds of nickel.  
Trudy Inst.khim.AN Gruz. SSR 16:3-8 '62. (MIRA 16:4)  
(Nickel compounds)

AKHOBADZE, V.

Soviet people are solving technical problems. NTO 5 no.3:  
34-36 Mr '63. (MIRA 16:4)

1. Uchenyy sekretar' Tsentral'nogo pravleniya Nauchno-tekh-  
nicheskogo obshchestva zheleznodorozhnogo transporta.  
(Railroads—Technological innovations)

GRUZ SSR / Human and Animal Physiology. Nervous System. T

Abs Jour: Ref Zhur-Biol., No 5, 1958, 22650.

Author : ~~Akhobadze, V. A.~~

Inst : Institute of Clinical and Experimental Cardiology.

Title : Electroencephalographic Investigations in Hypertensive Disease.

Orig Pub: Tr. in-t klinich. i eksperim. kardiol. A. N. Gruz SSR, 1956 (1957), 4, 361-367.

Abstract: Changes in the EEG from the Convex surface of the brain in the progress of hypertensive disease consisted in the replacement of low voltage rhythm of 15-30 oscillations per second, as observed in the initial phase, by slower rhythms. There were no changes in the initial stages in the basal segments, but the aggravation of the disease was followed by an irritation, particularly intense in the second phases.

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AKHOBADZE, V. A., Candidate of Med Sci (diss) -- "The bioelectric activity of the brain in hypertension". Tbilisi, 1959, published by the Acad Sci Georgian SSR.

44 pp (Tbilisi State Med Inst), 200 copies (KL, No 21, 1959, 119)

MCHEDLISHVILI, G.I.; AKHOBADZE, V.A.

Dynamics of changes in cerebral circulation in traumatic brain edema;  
experimental study. Vop. neirokhir 24 no. 2:13-19 Mr-Sp '60.

(MIRA 14:1)

(BRAIN--BLOOD VESSELS) (EDEMA)

MCHEDLISHVILI, G.I.; AKHOBADZE, V.A.; ORMOTSADZE, L.G. (Tbilisi)

Dynamics of disorders of brain blood circulation and their compensation following temporary occlusion of the aorta.

Pat. fiziol. i eksp. terap. 6 no.3:17-23 My-Je'62

(MIRA 17:2)

1. Iz otdela patologicheskoy fiziologii i morfologii nervnoy sistemy (zav. - pochetnyy akademik AN GruzSSR V.V. Voronin [deceased]) Instituta fiziologii AN GruzSSR.

MCHEDLISHVILI, G.I.; AKHOBADZE, V.A.; ORMOTSADZE, L.G.;

Hemodynamic mechanisms in the compensation of cerebral circulation  
during temporary occlusion of the cranial (superior) vena cava.  
Fiziol.zhur. 48 no.6:684-691 Je '62. (MIRA 15:8)

1. From the Institute of Physiology, Georgian S.S.R. Academy of  
Sciences, Tbilisi.

(BRAIN--BLOOD SUPPLY) (VENAE CAVA)



AKHOBADZE, V.A.

Bioelectric activity of the cerebral cortex in atherosclerosis.  
Trudy Inst. klin. i eksper. kard. AN Gruz. SSR 8:93-95 '62.  
(MIRA 17:7)

1. Institut kardiologii AN GruzSSR, Tbilisi.

MCHEDLISHVILI, G.I.; AKHOBADZE, V.A.; ORMOTSADZE, L.G.

Dynamics of disorders of the cerebral circulation and  
their compensation in a temporary occlusion of the aorta.  
Trudy Inst.klin. i eksper. kard. AN Gruz. SSR 8:543-549  
'63.

Experimental investigations of cerebral circulation in  
a temporary occlusion of the cranial (superior) vena  
cava. Ibid.:537-541 (MIRA 17:7)

1. Institut kardiologii i institut fiziologii AN  
GruzSSR, Tbilisi.

AKHOBADZE, V.S.

In the Scientific and Technical Society. Biul.tekh.-ekon.Inform.  
Nauch.-tekh.sov.Min.putei soob. no.1:94 '63. (MIRA 17:1)

AKHOBADZE, V. V.

"Gruzinskiye narodnye trudovye pesni 'naduri'."

report submitted for 7th Intl Cong, Anthropological & Ethnological Sciences,  
Moscow, 3-10 Aug 64.

AKHONIN, F. I.

Akhonin, F. I. "Geometrical positions of the stator current of an asynchronous motor operating in a Kramer cascade", Sbornik nauch.-tekhn. statey Khar'k. elektrotekhn. in-ta, Issue 7, 1948, p. 310-18.

So: U-3261, 10 April 53, (Letopis 'Zhurnal 'nykh Statey, No. 12, 1949).

LEVKOVSKIY, N.; KUZNETSOV, Ye.; AKHPOLOV, I.

Maintenance and repair of refrigerated motortrucks. Avt.  
transp. 43 no.12:22-24 D '65. (MIRA 18:12)

AKHPOLOV, I.K., inzh.; VLASKO, Yu.M.

Operational requirements for dump trucks and tractor trains  
carrying loads of loose materials. Stroi. i dor. mash. 9  
no.9:22-25 S '64. (MIRA 17:11)

AKHRABIYAN, B.A.; GULIYEV, G.A.; SHIRINOV, A.M.

New data on reservoir properties of Paleogene-Miocene sediments  
in the Caspian monocline. Neftegaz. geol. i geofiz. no.11:  
19-22 '65. (MIRA 18:12)

1. Institut geologii AN AzSSR.



AKHRA MEYEV, L.V.

Protection of water heating equipment using chlorinated  
fiber and mass. Energetik 11 no.11:19 N '63.  
(MIRA 16:11)

AKSEL'RUD, N.V.[deceased]; AKHRAMEYEVA, T.I.

Basic chlorides and lutetium hydroxide. Zhur. neorg. khim. 7  
no.8:1998-2001 Ag '62. (MIRA 16:6)

1. Institut obshchey i neorganicheskoy khimii AN UkrSSR.  
(Chlorides) (Lutetium compounds)

DRYAGINA, I.V.; AKHRAMOVA, V.F.

Vitality and fertility of the vegetative offspring of gladiolus corms which were exposed to chronic radiation in a  $\gamma$ -field. Nauch. dokl.vys.shkoly; biol.nauki no.4:98-102 '62. (MIRA 15:10)

1. Rekomendovana katedroy genetiki i seleksii Moskovskogo gosudarstvennogo universiteta im. Lomonosova.  
(PLANTS, EFFECT OF GAMMA RAYS ON)(GLADIOLUS)

ZAGLYADIMOV, Dmitriy Petrovich; PETROV, Aleksandr Petrovich;  
SERGEYEV, Yevgeniy Stepanovich; AKHRAMOVICH, L.K.,  
retsenzent; VARGIN, S.N., retsenzent; YERMAKOV, A.A.,  
retsenzent; KOZAK, V.A., retsenzent; MODZOLEVSKIY,  
I.V., retsenzent; PERSHIN, B.F., retsenzent; PIVENSHTeyN,  
D.I., retsenzent; PROKOF'YEV, A.G., retsenzent; SMETANIN,  
A.I., retsenzent; SHESTAKOV, A.I., retsenzent; RYSHUK,  
N.S., red.

[Organization of traffic in railroad transportation] Orga-  
nizatsiia dvizheniia na zheleznodorozhnom transporte.  
Izd.4. Moskva, Transport, 1964. 542 p. (MIRA 18:1)

AUTHORS: Nesmeyanov, A. N., Member, Academy of Sciences, USSR, Pecherskaya, K. A., Akhramovich, A. N.,  
Minakova, L. M. SOV/20-121-4-24/54

TITLE: Stereochemistry of  $\sigma, \pi$ - Conjugation (Stereokhimiya  $\sigma, \pi$ -sopryazheniya) Autooxidation of Rigid Allyl Systems (Avtookisleniye zhestkikh allil'nykh sistem)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 121, Nr 4, pp. 660 - 663 (USSR)

ABSTRACT: In earlier papers the authors proved (Ref 1) that in rigid (zhestkiy) bicyclic structures C — H and C — Hg-bindings on the top of the bridge of such structures, in an  $\alpha$ -position to the carbonyl, are not activated by the carbonyl. Neither is under acid action the mercury of  $\alpha$ -chloromercury camphenylone and of mercury-bis- $\alpha$ -camphenylone is substituted nor does an exchange for  $Hg^{2+}$  and  $HgCl_2$  take place. In camphenylone the  $\alpha$ -hydrogen atom is neither treated with nitrous acid nor sulfonated nor brominated. The  $\sigma, \pi$ -conjugation of the system A-C-C=O is usually eliminated when the  $\sigma$ -axis of binding is at right angle to the  $\pi$ -surface.

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Stereochemistry of  $\sigma, \pi$ -Conjugation. Autooxidation  
of Rigid Allyl Systems

SOV/20-121-4-24/54

The aim of this paper is it to clarify if there are similar conditions for the elimination of H-C-C=C-conjugation as were proved by the authors for H-C-C=O-conjugation. For this purpose they investigated such terpene hydrocarbons with respect to their capacity of being oxidizable. In terpene hydrocarbons (thanks to a methylene bridge) the C — H-binding in  $\alpha$ -position to the double binding seems to be spatially attached to the latter, namely bornylene (I), camphene (II) and  $\delta$ -fenchene. Referring to the above mentioned these hydrocarbons are compounds with a rigid structure. It could be proved that these hydrocarbons do not absorb any oxygen after they are kept many hours at temperatures of 40, 60 and 80° in presence of such active initiators as cobalt and manganese stearates. After oxidation they were recovered from the solution in unchanged state. Under such conditions non-rigid allyl systems are easily oxidized by molecular oxygen be it in presence or absence of an initiator. This fact was experimentally proved in the case of related compounds with a non-rigid structure. Thus it could be proved by means of experiments that in the

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Stereochemistry of  $\sigma, \pi$ -Conjugation. Autooxidation  
of Rigid Allyl Systems

SOV/2o-121-4-24/54

case of the homolytical  $\sigma, \pi$ -conjugation the influence of  
the same spatial factors occurs as in heterolytical con-  
jugations. There are 1 table and 15 references, 7 of which  
are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR  
(Institute of Elemental-Organic Compounds, AS USSR) Belorusskiy  
gosudarstvennyy universitet im.V.I.Lenina (Belorussian State  
University imeni V.I.Lenin)

SUBMITTED: April 21, 1958

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~~AKHRAMOVICH, L.K., inzh., doktor tekhn. nauk; BERNGARD, K.A., kand. tekhn. nauk; FEDENEV, G.S.; AL'TERMAN, C.L., red.; BOBROVA, Ye.N., tekhn. red.~~

[Advanced methods of dispatching in train traffic] Peredovye metody  
dispetcherskogo komandovaniia dvizheniem poezdov. Moskva, Gos.  
transp. shel-dor. izd-vo, 1958. 107 p. (MIRA 11:7)  
(Railroads—Train dispatching)



CHERNYAKHOVSKAYA, Neonila Ivanovna: PRERUBOVICH, R.T., ed. red.  
POLTAVSKAYA, S.V., red.

[Industrial development and the condition of the working  
class in Afghanistan] Razvitie promyshlennosti i polozhe-  
nie rabochoego klassa Afganistana. Moskva, Nauka, 1985.  
168 p. (MIRA 18:11)

AKHRAMOVICH, Roman Timofeyevich; DVORYANKOV, N.A., otv. red.; GASRATYAN, M.A.,  
red. izd-va; TSVETKOVA, S.V., tekhn. red.

[Afghanistan after the Second World War; historical study] Afganistan  
posle vtoroi mirovoi voyny; ocherk istorii. Moskva, Izd-vo vostochnoi  
lit-ry, 1961. 175 p. (MIRA 14:8)  
(Afghanistan—Politics and government) (Afghanistan—Economic  
conditions)

AKHRAOVSKIY, N.N.

Land mollusks in the region of the village of Gnishik in Soviet  
Armenia. Zool.sbor. no.6:127-183 '49. (MLRA 9:8)  
(Armenia--Snails)

AKHRAP, S. K.

IVANOV, V.G., assistant; AKHRAP, S.K., assistant.

Generalization of findings on damming river channels with rock  
fill. Trudy MEI no.19:294-328 '56. (MIRA 10:1)

1. Kafedra proizvodstva rabot po stroitel'stvu gidrotekhnicheskikh  
sooruzheniy. (Dams)

TERENT'YEV, V.A., inzh.; AKHRAP, S.K., inzh.

Concrete work in construction of the Bratsk Hydroelectric Power  
Station. Gidr. stroi. 33 no.11:5-12 N '62. (MIRA 16:1)  
(Bratsk Hydroelectric Power Station—Concrete construction)

AKHRARKHODZHAYEV, A. A., Cand Med Sci -- (diss) "Materials on the study of the pathology and clinic of pulmonary hemorrhage and hemoptysis in tubercular patients in Tashkent." Alma-Ata, 1960. 14 pp; (Kazakhstan State Medical Inst); 350 copies; price not given; (KL, 25-60, 138)

AKHARKHODZHAYEV, A.A.

А. А. Ахрарходжаев защитил 14/VI 1960 г. в Совете Казахского медицинского института диссертацию на тему «Материалы по изучению патологии и клиники легочных кровотечений и кровохарканий у больных туберкулезом в Ташкенте».

Клинически и другими методами исследований изучены климатометеорологические особенности, оказывающие отрицательное влияние на организм больного туберкулезом и провоцирующие легочные кровотечения в Ташкенте. Указаны пути эффективной терапии и профилактики легочных кровотечений.

Candidate of Medical Sciences

Dissertations approved by the Higher Attestation Commission in  
January and February of 1961. Terap. arkh. no.6:117-121 '61

ARKHARKH

ALIMOV, Sh.A.; AKHRARKHODZHAYEV, A.A.

Therapy of pulmonary tuberculosis in elderly persons. Trudy  
TSIU 63:118-122 '63. (MIRA 17:9)

1. Kafedra legochnogo tuberkuleza Tashkentskogo instituta  
usovershenstvovaniya vrachey.



AKHRAROV, A.

~~AKHRAROV, A.~~  
Climatotherapy in the compound treatment of functional diseases  
of the nervous system. Sbor.trud.Uz.gos.nauch.-issl.inst.kur. i  
fizioter. 17:84-87 '62. (MIRA 17:7)

S/058/63/000/002/037/070  
A062/A101

AUTHORS: Semenchenko, V. K., Akhrarov, S.

TITLE: Investigation on the dielectric permittivity of double liquid systems in the critical region

PERIODICAL: Referativnyy zhurnal, Fizika, no. 2, 1963, 11 - 12, abstract 2E65  
(In collection: "Vopr. sovrem. fiz. i matem.", Tashkent, AN UzSSR, 1962, 9 - 14)

TEXT: The dielectric permittivity ( $\epsilon$ ) was investigated near the critical lamination points of liquid systems of nitrobenzol-cyclohexane and nitrobenzol-nonane. The measurements were carried out by the beat method on the frequency 1 Mc/s with an accuracy 0.5% and thermostating to 0.01°C. It is established that at critical temperatures and concentrations the values of  $\epsilon$  pass through a sharply pronounced maximum. The magnitude and the sharpness of the maximum decrease as the concentration deviates from the critical value; also the temperature corresponding to the maximum is displaced. The results obtained confirm the view point of V. K. Semenchenko about the equivalency of the second-kind transitions and the

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Investigation on the dielectric permittivity of...  
critical phenomena.

S/058/63/000/002/037/070  
A062/A101

L. Filippov

[Abstracter's note: Complete translation]

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L 16200-63

Pr-4 RM/WW/WH

EPR/EFF(c)/EWT(m)/BDS/EWP(j)

AFFTC/ASD

PS-4/PC-4/

ACCESSION NR: AP3006538

S/0191/63/000/009/0033/0035

AUTHOR: Ahratova, Sh. K.

TITLE: Properties of glass-reinforced plastics based on fabrics from alkali glass

SOURCE: Plasticheskiye massy, no. 9, 1963, 33-35

TOPIC TAGS: glass fabric reinforced plastic, alkali glass fabric, satin weave fabric 8/3, finish, coupling agent, heat cleaning, finishing, GVS-9, VTAS, GVS-9 finish, VTAS finish, zinc nitrate, reinforcement, binder, PN-1, PN-1 resin, polyester, polyester resin, PN-1 polyester resin, binding strength, water resistance, steam resistance, weather resistance, salt water resistance

ABSTRACT: Plastics reinforced with alkali-glass fabric have been prepared. Satin fabric 8/3, heat-cleaned and finished with organo-silicon coupling agents GVS-9 or VTAS or with  $Zn(NO_3)_2$ , was used

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ACCESSION NR: AP3006538

as a reinforcement, and PN-1 polyester resin with added initiator and accelerator, as a binder. The fabric/binder ratio was 1/1. The results of the study are given in tables and a graph. The properties of plastics reinforced with alkali and alkali-free glass fabric finished with GVS-9 are similar. Thus the bending strengths of dry and wet plastics reinforced with alkali-glass fabric are 3222 and 2455 kg/cm<sup>2</sup>, respectively. The resistance of these plastics to water, steam, weather, and salt water is increased by the GVS-9 finish. The properties of plastics prepared from PN-1 resin and alkali-glass fabric finished with GVS-1 can be further improved by using a more effective organosilicon finish. Orig. art. has: 1 figure and 3 tables.

ASSOCIATION: none

SUBMITTED: 00

DATE ACQ: 30Sep63

ENCL: 00

SUB CODE: MA

NO REF SOV: 004

OTHER: 007

Card 2/2

AKHREM, A. A.

Acetylene derivatives. XCVIII.  $\alpha$ -Keto oxides and their transformations. 2. Oxidation of divinyl ketones by alkaline hydrogen peroxide. Synthesis of  $\alpha$ -keto oxides. N. Nazarov and A. A. Akhrem. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1950, 621-34; cf. *C.A.* 45, 7062e, 7569f, 7683d.  $\text{Me}_2\text{C}:\text{CHCOCH}:\text{CH}_2$  (b.p. 48° (cf. *C.A.* 36, 7469i) (280 g.) in 2 l. dioxane was treated with cooling (5°) with 1 l. 18%  $\text{H}_2\text{O}_2$  and 100 ml. 4 N NaOH added from separate funnels over 3 hrs.; after 0.5 hr. further stirring and neutralization with 105 ml. 10%  $\text{H}_2\text{SO}_4$  (trace of peroxide removed with  $\text{MnO}_2$ ), an  $\text{Et}_2\text{O}$  ext. yielded 200 g.  $\text{O}:\text{CH}_2\text{CH}:\text{COCH}:\text{CMe}_2\text{O}$  (I), b.p. 80°, b.p. 70°,  $n_D^{20}$  1.4560,  $d_4^{20}$  1.1188, whose semicarbazone, m. 150-0°, cannot be recrystd.; reaction of I with dry  $\text{HCl}$  in  $\text{Et}_2\text{O}$  requires over 14 days at room temp., while 41 g. I with 390 ml.  $\text{H}_2\text{O}$  at room temp. (5 days) gave on vacuum evapn. 12.5 g. 2,2-dimethyl-3,6-dihydroxytetrahydro-4-pyrone, m. 107° (from  $\text{CHCl}_3$ ), sublimed 85-7° at 0.1 mm., whose 2,4-dinitrophenylhydrazine, m. 208-8.5° (from  $\text{EtOH}$ ); simultaneously is also formed 21 g. of an apparent isomer of this pyrone, b.p. 118-19°,  $n_D^{20}$  1.4808,  $d_4^{20}$  1.2241, which on standing slowly deposits the product m. 107°; it is possible that the liquid is a mixt. of this substance with  $\text{Me}_2\text{C}:\text{CH}(\text{OH})\text{COCH}(\text{OH})\text{CH}:\text{OH}$ . I (37 g.) hydrolyzed 9 hrs. at 100° with  $\text{H}_2\text{O}$ , forms 37 g. undistillable sirup, which with  $\text{CHCl}_3$  yields 3.5 g. of the above pyrone, m. 107°, and about 30 g. above triol, a viscous sirup. The pyrone yields a diacetate (II) (from cold  $\text{Ac}_2\text{O}$ -pyridine), b.p. 95°,  $n_D^{20}$  1.4515,  $d_4^{20}$  1.1660, while

similar acetylation of the sirupy form gave a diacetate, b.p. 125-0°,  $n_D^{20}$  1.4585. Acetylation of the triol with  $\text{NaOAc}:\text{Ac}_2\text{O}$  at 100° gave a poor yield of II, b.p. 121.5-3.0°,  $n_D^{20}$  1.4620. Heating 5 g. I with 2.5 g.  $\text{Et}_3\text{NH}$  2 hrs. to 60-60° gave 4 g. 2,2-dimethyl-3-diethylamino-5-hydroxytetrahydro-4-pyrone, b.p. 133°,  $n_D^{20}$  1.5335, whose  $n$  changes on standing to 1.5462 in 9 days. Letting 7 g. I and 3.8 g.  $\text{Et}_3\text{NH}$  stand 2 days and heating the soln. with 10 g.  $\text{Ac}_2\text{O}$ , 2 hrs. at 80°

gave 4.5 g. monoacetate (II), probably  $\text{O}:\text{CMe}_2\text{C}(\text{NEt}_2):\text{C}:$

$(\text{OAc})\text{CH}:\text{CH}$ , pink liquid, b.p. 72°,  $n_D^{20}$  1.5330,  $d_4^{20}$  1.0357. Slow addn. of 4.0 g.  $\text{Et}_3\text{NH}$  to 5 g. I at 10° and standing overnight in the cold gave an undistillable tar; extrn. with  $\text{Me}_2\text{CO}$  yielded 0.1 g.  $\text{C}_8\text{H}_{14}\text{O}_2\text{N}$ , m. 100°, possibly a dehydration product of 2,2-dimethyl-3-ethylamino-5-hydroxy-4-pyrone. While I does not react with  $\text{H}_2\text{S}$  in the cold without a catalyst, reaction in the presence of  $\text{NaOAc}$  is vigorous (best in dioxane), giving an undistillable oil having a sulfide link and some S; the same sulfide forms in abs.  $\text{MeOH}$ , when  $\text{Et}_3\text{N}$  is the catalyst, in a smooth reaction at -70°. I could not be made to add  $\text{MeOH}$  in the presence of either  $\text{MeONa}$  or dry  $\text{HCl}$ . Oxidation of  $\text{Me}_2\text{C}:\text{CHCO}:\text{CH}:\text{CH}_2$  (80 g.) in 100 ml.  $\text{AcOH}$  with 300 g.  $\text{Ac}_2\text{O}:\text{H}$  contg. 7.18% active O with ice cooling, followed by 3 days

OVCY

A. A. AKHREM

Nov 51

USSR/Chemistry - Oxidation of Olefins

"Life and Works of Nikolay Ale<sup>K</sup>androvich Prilezhayev," A. A. Akhrem, Ye. N. Prilezayeva,  
A. P. Meshcheryakov

"Zhur Obshch Khim" Vol XXI No 11, pp 1925-1931

Presents brief general biography of chemist N. A. Prilezhayev (1872 - 1944) and lists of his scientific works. Devotes considerable discussion to Prilezhayev's work on rules governing oxidation of olefinic double bonds with benzoyl hydroperoxide and synthesis of the compds involved.

PA 194T41

AKHREM, A. A. and NAZAROV, I. N.

"Acetylene Derivatives. 132. Alpha-Keto Oxides and Their Transformations,"  
Zhur. ob. khim., 22 (84), No.3, 1952

Inst. Organic Chem., AS USSR



NAZAROV, I.N.; AKHREM, A.A.; TISHCHENKO, I.G.

Acetylene derivatives. 167.  $\alpha$ -keto oxides and their conversions.  
Part IV. Oxides of 2-methyl-1, 4-hexadiene-3-one, 5-methoxy-2-methyl-  
1-hexene-3-one, and of 1-methoxy-2-methyl-4-hexene-3-one. Zhur.ob.  
khim. 25 no.4:708-725 Ap '55. (MIRA 8:7)

1. Institut organicheskoy khimii Akademii Nauk SSSR i Belorusskiy  
Gosudarstvennyy universitet. (Ketones) (Oxides)

NAZAROV, I.N.; AKHREM, A.A.; TISHCHENKO, I.G.

Acetylene derivatives. 168.  $\alpha$ -keto oxides and their conversions. Part V. Oxides of 1,4-hexadiene-3-one, 5-methyl-2, 5-heptadiene-4-one, and of 2-methoxy-5-methyl-5-heptene-4-one. Zhur.ob.khim. 25 no.4:725-734 Ap '55.  
(MLRA 8:7)

1. Institut organicheskoy khimii Akademii Nauk SSSR i Belorusskiy Gosudarstvennyy universitet. (Ketones) (Oxides)

A preparative method for the synthesis of cyanohydrins. I. N. Nozarov, A. A. Akhrem, and A. V. Kamernitskiy (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Zhur. Obshchei Khim.* 25, 1345-54 (1955).—A convenient synthesis of cyanohydrins was developed based on exchange reaction of  $\text{Me}_2\text{C}(\text{OH})\text{CN}$  (I) with other ketones and aldehydes. The yields of the products depend on the soly. and disocn. constants of the products. Thus, I,  $b_p$  66-7°,  $n_D^{20}$  1.400 (17 g.), and 14.4 g.  $\text{MeEtCO}$  mixed with 5 ml.  $\text{MeOH-K}_2\text{CO}_3$ , kept overnight at 20°, then slightly acidified with  $\text{H}_2\text{SO}_4$  to Congo red, distd. at 55-60° to remove  $\text{MeOH}$  and  $\text{Me}_2\text{CO}$ , treated with 7 ml. catalyst soln. and again kept overnight, gave on distn. 13.3 g.  $\text{MeEtC}(\text{CN})\text{OH}$ , still contaminated with the starting material (distn. was ineffective). I (51 g.), 22.8 g.  $\text{Pr}_2\text{CO}$ , and 25 ml.  $\text{MeOH-K}_2\text{CO}_3$  allowed to react as above (in 2 steps) gave 15.8 g.  $\text{Pr}_2\text{C}(\text{CN})\text{OH}$ ,  $b_p$  84-4.5°,  $n_D^{20}$  1.4335,  $d_4^{20}$  0.9040. iso- $\text{Pr}_2\text{CO}$  (22.8 g.) heated with 51 g. I and 20 ml.  $\text{MeOH-K}_2\text{CO}_3$ , 5 hrs. at 65-70°, the mixt. kept overnight at 20°, acidified and distd. gave a residue of 20 g. iso- $\text{Pr}_2\text{C}(\text{CN})\text{OH}$ , m. 59-9.5°.  $\text{AcCH}_2\text{CO}_2\text{Et}$  (39 g.), 70.5 g. I, and 45 ml.  $\text{MeOH-K}_2\text{CO}_3$  kept overnight at 20°, acidified and evapd. *in vacuo* gave 30.6 g. Et acetoacetate cyanohydrin,  $b_p$  87.5-8°,  $n_D^{20}$  1.4338,  $d_4^{20}$  1.0323.  $\text{PrCHO}$  (18 g.), 63.75 g. I, and 20 ml.  $\text{MeOH-K}_2\text{CO}_3$  kept overnight at 20° gave 20.4 g.  $\text{PrCH}(\text{CN})\text{OH}$ ,  $b_p$  73-4°,  $n_D^{20}$  1.4220,  $d_4^{20}$  0.9397. Similarly 20 g.  $\text{EtCHO}$  and 85 g. I with 50 ml.  $\text{MeOH-K}_2\text{CO}_3$  gave 20 g.  $\text{EtCH}(\text{CN})\text{OH}$ ,  $b_p$  62-4°,  $n_D^{20}$  1.4150,  $d_4^{20}$  0.9010. I (42.5 g.) and 33 g. 35-7% formalin with 0.6 g.  $\text{K}_2\text{CO}_3$  in 5 ml.  $\text{H}_2\text{O}$  kept overnight at 0°, acidified, evapd. and extd. with  $\text{Et}_2\text{O}$  gave 20 g.  $\text{CH}_2(\text{CN})\text{OH}$ ,  $b_p$  77-0°,  $n_D^{20}$  1.4108; paraformaldehyde (13.2 g.) and 34 g. I at 40-2° were treated with 10 ml.  $\text{MeOH-K}_2\text{CO}_3$ , kept 1.5 hrs. at 20° and acidified, evapd. and extd. with  $\text{Et}_2\text{O}$  to yield 18.1 g.  $\text{CH}_2(\text{CN})\text{OH}$ ,  $b_p$  76.5-8°; this with concd.  $\text{HCl}$  enters a vigorous reaction and yields after heating 2 hrs. on a steam bath glycolic acid.  $\text{BrH}$  (31.8 g.) and 25.5 g. I with 10 ml.  $\text{MeOH-K}_2\text{CO}_3$  kept overnight gave, after usual treatment, 35.8 g.  $\text{PhCH}(\text{OH})\text{CN}$ , which could not be recrystd. successfully; with concd.  $\text{HCl}$  this readily gave mandelic acid. Cyclohexanone (78.4 g.) and 136 g. I with 20 ml.  $\text{MeOH-K}_2\text{CO}_3$  after standing overnight at 20° gave 85.9 g.  $(\text{CH}_2)_6\text{C}(\text{OH})\text{CN}$ , m. 34-6°, which with concd.  $\text{HCl}$  gave 1-hydroxycyclohexanecarboxylic acid, m. 108-9°;  $\text{Et}_3\text{N}$  or piperidine catalysts gave the same result at 0.01 mole per 1 mole I. 1-Methylcyclohexanone (22.4 g.) and I similarly gave 25.1 g. 1-methylcyclohexanone cyanohydrin,  $b_p$  92.5-3.5°,  $n_D^{20}$  1.467, which on freezing gave 1 isomer, m. 53.5-4°, and another isomer,  $b_p$  99-100.5°,  $n_D^{20}$  1.4671. 1-Methylcyclopentanone (4.9 g.) similarly gave 4.4 g. corresponding cyanohydrin,  $b_p$  85-6°,  $n_D^{20}$  1.4602. Similarly 12.8 g. 2,2-dimethyltetrahydro-4-pyranone gave 10.1 g. cyanohydrin, m. 88-9°, while 14.1 g. 1,2,5-trimethyl-4-piperidone gave 16.6 g. cyanohydrin, m. 127-9°, from aq. soln. of I without a catalyst. Similarly 1,3-dimethyl-4-piperidone and I gave the cyanohydrin, m. 84.5-6°. 1-benzyl-Decahydronaphthalenone and I required the use of  $\text{MeOH-K}_2\text{CO}_3$  and gave about 55% cyanohydrin, m. 80.5-1.5°. Also in *J. Gen. Chem. U.S.S.R.* 25, 1291-5 (1955). (Engl. translation).  
G. M. Kosolapoff

77-0°,  $n_D^{20}$  1.4108; paraformaldehyde (13.2 g.) and 34 g. I at 40-2° were treated with 10 ml.  $\text{MeOH-K}_2\text{CO}_3$ , kept 1.5 hrs. at 20° and acidified, evapd. and extd. with  $\text{Et}_2\text{O}$  to yield 18.1 g.  $\text{CH}_2(\text{CN})\text{OH}$ ,  $b_p$  76.5-8°; this with concd.  $\text{HCl}$  enters a vigorous reaction and yields after heating 2 hrs. on a steam bath glycolic acid.  $\text{BrH}$  (31.8 g.) and 25.5 g. I with 10 ml.  $\text{MeOH-K}_2\text{CO}_3$  kept overnight gave, after usual treatment, 35.8 g.  $\text{PhCH}(\text{OH})\text{CN}$ , which could not be recrystd. successfully; with concd.  $\text{HCl}$  this readily gave mandelic acid. Cyclohexanone (78.4 g.) and 136 g. I with 20 ml.  $\text{MeOH-K}_2\text{CO}_3$  after standing overnight at 20° gave 85.9 g.  $(\text{CH}_2)_6\text{C}(\text{OH})\text{CN}$ , m. 34-6°, which with concd.  $\text{HCl}$  gave 1-hydroxycyclohexanecarboxylic acid, m. 108-9°;  $\text{Et}_3\text{N}$  or piperidine catalysts gave the same result at 0.01 mole per 1 mole I. 1-Methylcyclohexanone (22.4 g.) and I similarly gave 25.1 g. 1-methylcyclohexanone cyanohydrin,  $b_p$  92.5-3.5°,  $n_D^{20}$  1.467, which on freezing gave 1 isomer, m. 53.5-4°, and another isomer,  $b_p$  99-100.5°,  $n_D^{20}$  1.4671. 1-Methylcyclopentanone (4.9 g.) similarly gave 4.4 g. corresponding cyanohydrin,  $b_p$  85-6°,  $n_D^{20}$  1.4602. Similarly 12.8 g. 2,2-dimethyltetrahydro-4-pyranone gave 10.1 g. cyanohydrin, m. 88-9°, while 14.1 g. 1,2,5-trimethyl-4-piperidone gave 16.6 g. cyanohydrin, m. 127-9°, from aq. soln. of I without a catalyst. Similarly 1,3-dimethyl-4-piperidone and I gave the cyanohydrin, m. 84.5-6°. 1-benzyl-Decahydronaphthalenone and I required the use of  $\text{MeOH-K}_2\text{CO}_3$  and gave about 55% cyanohydrin, m. 80.5-1.5°. Also in *J. Gen. Chem. U.S.S.R.* 25, 1291-5 (1955). (Engl. translation).  
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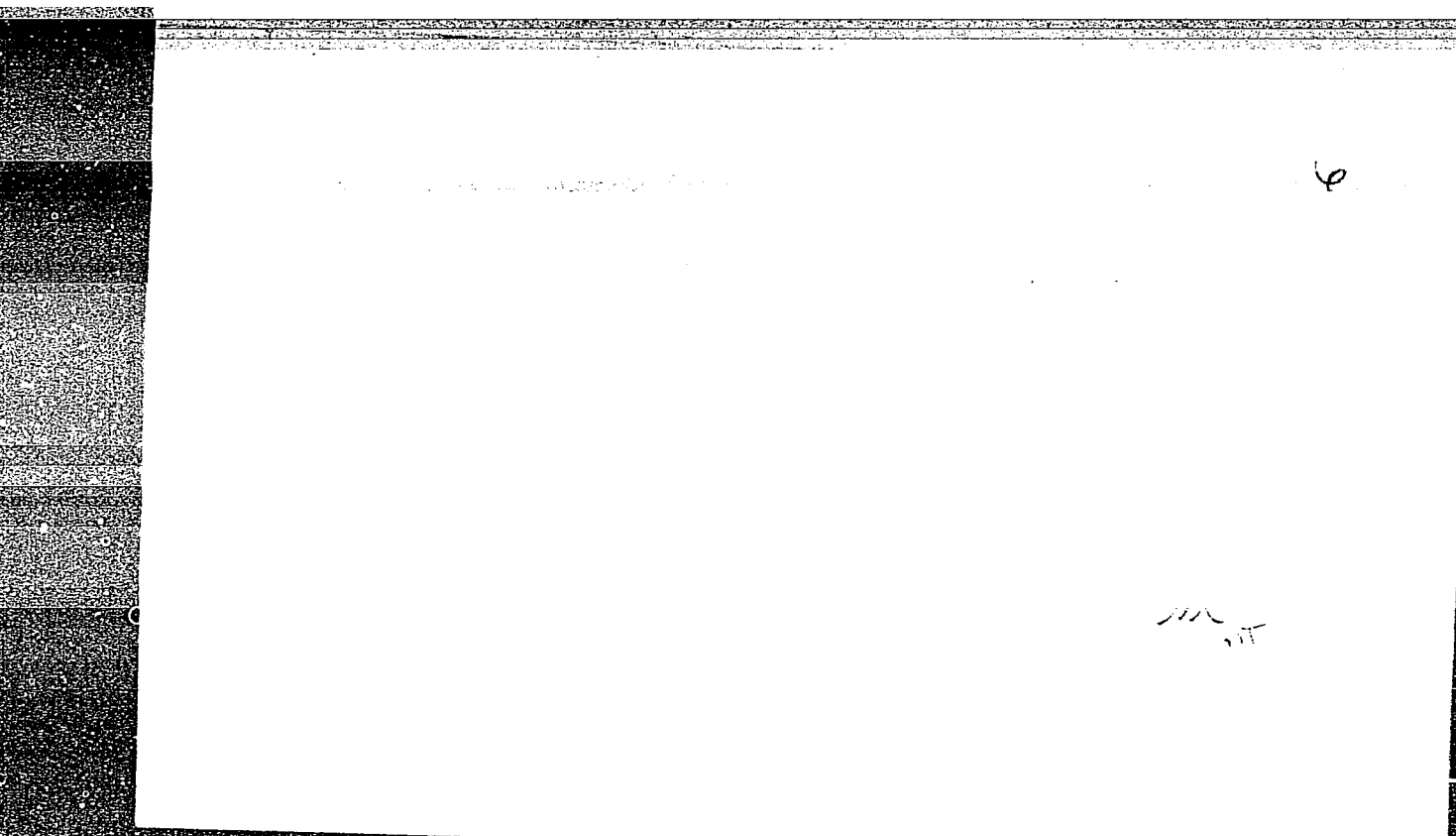
Synthesis of steroid compounds and related to them substances.  
Part 33. Simple analogs of corticosteroids. Part 1. Methods for  
the introduction of dioxyacetic, glyceric, and dioxypropanecarbo-  
xylic side chains into cyclic compounds. Zhur.ob.khim. 26 no,4:  
1186-1201 Ap '56. (MLRA 9:8)

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AKHREM, A.A.

62-1-12/21

**AUTHORS:**

Nazarov, I. N.; Akhrem, A. A.; Kokhomskaya, V. V.

**TITLE:**

Alpha-Ketooxides. Part 8. Conversions of Alpha-Dioxide of Beta, Beta-Dimethyl Divinyl Ketone (Alfa-Ketookisi. Soobshcheniye 8. Prevrashcheniya alfadiokisi beta, beta-dimetildivinylketona)

**PERIODICAL:**

Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1957, No. 1, pp. 80-90 (U.S.S.R.)

**ABSTRACT:**

This report is devoted to the study of the reaction occurring between alpha-ketodioxide and alcohols, acetic acid, amines and other compounds containing active hydrogen. Hydrolysis of alpha-ketooxide with water at room temperature leads to the formation of 2,2-dimethyl-3,5-dioxytetrahydro-4-pyrone in two stereoisomeric forms - crystalline and liquid. Hydrogenation of 2,2-dimethyl-3,5-dioxytetrahydro-4-pyrone with hydrogen at 120 atm. in the presence of Raney's nickel gives a high yield of 2,2-dimethyl-3,4,5-trioxytetrahydropyran which easily acetylates under the effect of acetic anhydride into a certain

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## Alpha-Ketooxides. Part 8

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triacetate. Hydrogenation of alpha-ketodioxide in the presence of Raney's Ni at room temperature produces a mixture from which the authors separated 2-isopropyl-4-oxytetrahydrofuran-3-on and 2-isopropyltetrahydrofuran-3-on.

The reaction of alpha-ketodioxide with ice-cold acetic acid and acetic anhydride at 150° forms diacetate having a furan structure. Heating of the alpha-ketodioxide with methyl alcohol at 250° forms a crystalline product which by its composition corresponds to 2-(alpha-methoxy)-isopropyl- $\Delta^4$  dihydrofuran-3-on. The reaction of ketodioxide with soda malonic ester at - 5° yields a product of undetermined structure. This product could not be separated individually because it decomposes without distillation at a bath temperature of 203° and pressure of 0.01 mm.

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There are 4 Slavic references.

Alpha-Ketooxides. Part 8

62-1-12/21

**ASSOCIATION**

Academy of Sciences USSR, Institute of Organic Chemistry imeni  
N. D. Zelinskiy and Academy of Sciences Byelorussian-SSR,  
Institute of Chemistry

**PRESENTED BY:**

**SUBMITTED:**

October 26, 1955

**AVAILABLE:**

Library of Congress

Card 3/3

*Akhrem, A.A.* 20-3-18/52

**AUTHORS:** Batuyev, M. I., Akhrem, A. A., Matveyeva, A. D.,  
and Nazarov, I. N., Academician (~~Deceased~~)

**TITLE:** Optical Investigation of Conformations of Cis- and Trans-2-  
-Methyl-1-ethylcyclohexanols (Opticheskoye issledovaniye kon-  
formatsiy tsis- i trans-2-metil-1-etiltsiklogeksanolov)

**PERIODICAL:** Doklady AN SSSR, 1957, Vol. 117, Nr 3, pp. 423-426 (USSR)

**ABSTRACT:** 1.) According to recent investigations cyclohexane mainly ex-  
ists in a "chair"-like (kresloobraznaya) form, which possesses  
a minimum of energy. The C--H bindings of this form may be  
placed at two groups: a) those which are parallel to the OZ-  
axis ("a" = axial bindings) and b) those which form an angle  
of  $\pm 19,5^\circ$  together with the OXY-surface ("e" = equatorial  
bindings). Because of the not great repelling powers between  
the hydrogen atoms the "chair"-like form is preferred with  
respect to the energy. For, in the "tub"-like ("vannoobraznaya")  
form the distances of each equatorial hydrogen atom ( $\sim 1,83 \text{ \AA}$ )  
are smaller, than the sum of two Van-der-Waal's radii.  
Khassel (ref. 1) has formulated a rule: in the series of the  
poly-substituted cyclohexanes the isomere with the greatest num-  
ber of equatorial substituents is most steady.

Card 1/4 2.) In the thirties Chiurdoglu (ref. 8) has identified the

Optical Investigation of Conformations of Cis- and Trans-2- 20-3-18/52  
-Methyl-1-ethylcyclohexanols.

cis- and trans-isomeres and others of the cis- and trans-dimethylcyclohexanols, without distinguishing here the conformations. Two of the authors of the present work (ref. 9) have synthesized the substances (I) and (II) mentioned in the title and transformed them on to the known pair of cis- and trans-1.2-dimethylcyclohexanols (III) and (IV). But their "conformation" cannot be defined exactly chemically. Here, the problem is investigated by means of the method of the combination-light-scattering, and for both substances mentioned in the title spectra were found out.

3.) Guiding principles experimentally proved a.) - g.) served the authors for the investigation of the obtained optical data.

4.) Cis- and trans-2-methyl-1-ethylcyclohexanols (I) and (II) form an intermolecular hydrogen compound in the liquid phase. This is expressed in the spectra by the fading of the frequency-band of the hydroxyl group. In solutions of these substances the faded bands disappear, because the intermolecular hydrogen bindings within the solutions are opened. The C -- OH-binding is equatorial in the isomere I, which has a frequency of the hydroxyl group  $3604\text{ cm}^{-1}$ , and axial in the isomere II with a frequency of that group  $3619\text{ cm}^{-1}$ .

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Optical Investigation of Conformations of Cis- and Trans-2-Methyl-1-ethylcyclohexanols.

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5.) The pulsating frequency in the spectra of the epimeres I and II is, as well in the liquid state as in solutions not single, but triplicated. The most intense frequency of the isomere I is  $682\text{ cm}^{-1}$ , of the isomere II  $693\text{ cm}^{-1}$ . The first belongs to the cis-, the latter to the trans-isomere. These frequencies remain preserved in the spectra of the solutions. Each of them occurs in the spectrum of the other substance with a weakened intensity. Because, as is said, the C--OH binding at the isomere I (= cis-isomere) is equatorial, whilst at the isomere II (= trans-) it is axial, isomere I is an epimere ep, and isomere II - an epimere ee (apart from admixtures of other conformations).

6.) This is confirmed, too, by data on the frequencies of the C--O bindings, as in the spectrum of the isomere I the frequency system within the range concerned is, compared to the spectrum of the isomere II, removed to the side of short wave-length.

7.) By the isomeres I and II the components of the molecules (ethyl- and methyl radicals, hydroxyl) possess a freedom of rotation around the single bindings. This, apparently, is the source of their conversion transformations and of the appearance of small quantities of unsteady, tub-like conformations,

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Optical Investigation of Conformations of Cis- and Trans-2-  
-Methyl-1-ethylcyclohexanols. 20-3-18/52

equipped with a pulsating frequency (apparently higher than  $802\text{ cm}^{-1}$ ), beside the mentioned two principle conformations. There are 1 figure, and 19 references, 7 of which are Slavic.

ASSOCIATION: ~~Institute~~ for Mineral Fuels, Institute for Organic Chemistry  
imeni N. D. Zelinskiy AN USSR (Institut goryuchikh iskopaye-  
mykh, Institut organicheskoy khimii im. N. D. Zelinskogo  
Akademii nauk SSSR).

SUBMITTED: August 17, 1957

AVAILABLE: Library of Congress

Card 4/4

62-58-5-17/27

AUTHORS: Nazarov, I. N., Akhrem, A. A., Kamernitskiy, A. V.

TITLE: Stereochemistry of Nucleophilic Addition to Carbonyl-Group  
Reactions of the 2-Methylcyclohexanone( Stereokhimiya  
reaktsiy nukleofil'nogo prisoyedineniya po karbonil'noy gruppe.  
Reaktsii 2-metiltsiklogeksanona)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk,  
1958, Nr 5, pp. 631 - 633 (USSR)

ABSTRACT: There are almost no references in the respective publications  
with respect to the possibility of the stereo-specific progress  
of the reactions of 2-methylcyclohexanone with similar ke-  
tones, unless the reduction of the same by metals or complex  
metallic hydrides (Reference 2) is added. A mixture of acetylene-  
alcohols with prevalently thinly liquid isomer the configuration  
of which was not determined, is formed with the condensation  
of ketone with acetylene in liquid ammonia. The reaction of  
methyl-magnesium-iodide with ethylester of cyclohexanone-  
carboxylic-4-acid leads selectively to the ester of the trans-

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Stereochemistry of Nucleophilic Addition to Carbonyl-  
Group Reactions of the 2-Methylcyclohexanone

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-1-methylcyclohexanolcarboxylic-4-acid (Reference 4). Trans-2-chlorine-1-methylcyclohexanol (Reference 5) is formed when the interaction of methylmagnesium-iodide with 2-chlorine-cyclohexanone has taken place. With the reduction of the ketone by sodium (Reference 6) or by complex metallic hydrides, (Reference 7), however, the substituent taking place moves into the cis-position with respect to the already present substituent. Thus, the correlation of the cis-and transisomers forming with the reactions, is different. There are 1 figure, 1 table and 12 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR ( Institute for Organic Chemistry imeni N. D. Zelinskiy AS USSR)

SUBMITTED: December 19, 1957

1. Cyclic compounds--Chemical reactions    2. Stereochemistry--Applications  
3. Molecular structures--Test methods

Card 2/2

62-58-5-19/27

AUTHORS: Nazarov, I. M., Aleksandrova, G. V., Akhrem, A. A.

TITLE: Introduction of the Oxyacetone-Glycerin-and Dioxycarbon Side Chains in Cis- and Trans-Decalin-Derivatives (Vvedeniye oksiatsetonovoy, glitserinovoy i dioksikarbonovoy bokovykh tsepey v proizvodnyye tsis-i trans-dekalinov )

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1958, Nr 5, pp. 634 - 636 (USSR)

ABSTRACT: The present report deals with the conversions of the trans-1-ethinyl-1-decalol and of the cis-1-ethinyl-1-decalol and their acetates into compounds with acetone-, glycerin-and dioxycarbon -side-chains. Glycides and dibromoketol-methods were investigated for the purpose of the introduction of the glycerin-and dioxycarbon-side-chains into the molecule of the cis-and trans- $\alpha$ -dekalones. 6 stereochemical isomers of the cis-and trans-1-oxydecalylglycoles, 4 isomers of the oxydecalyl-ethylenoxide and 5 stereo-isomeric oxydecalylglycolic acids

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Introduction of the Oxyacetone-, Glycerin -and Dioxy- 62-58-5-19/27  
carbon Side Chains in Cis-and Trans-Decalin-Derivatives

were further separated. There are 7 references, 4 of which  
are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii  
nauk SSSR ( Institute for Organic Chemistry imeni N. D. Ze-  
linskiy AS USSR)

SUBMITTED: December 25, 1957

1. Cyclic compounds--Chemical reactions 2. Stereochemistry--Appli-  
cations 3. Molecular structure--Determination

Card 2/2

SOV/62-58-11-20/26

5(3)

AUTHORS:

Batuyev, M.I., Akhrom, A.A.,  
Matveyeva, A.D., Nazarov, I.N.

TITLE:

Optical Investigation of Cis- and Trans-2-Methyl-1-Acetyl  
Cyclohexanol Conformations  
(Opticheskoye issledovaniye konformatsiy tsis- i trans-2-metil-  
-1-atsetiltsiklogeksanolov)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958,  
Nr 11, pp 1389 - 1392 (USSR)

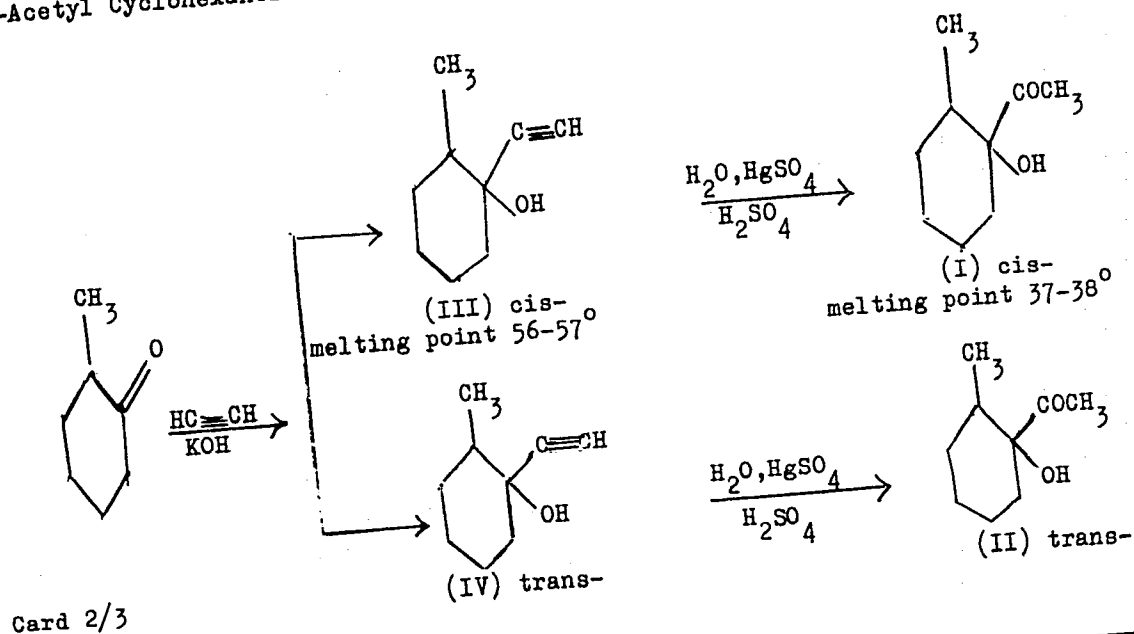
ABSTRACT:

In this brief report the authors described the investigation of  
the conformation of epimeric 2-methyl-1-acetyl cyclohexanols (I)  
and (II) obtained by means of hydration of the corresponding  
2-methyl-1-ethynyl cyclohexanols (III) and (IV) (Ref 2):

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Optical Investigation of Cis- and Trans-2-Methyl-1-Acetyl Cyclohexanol Conformations

SOV/62-58-11-20/26



Optical Investigation of Cis- and Trans-2-Methyl-  
-1-Acetyl Cyclohexanol Conformations

SOV/62-58-11-20/26

Physical properties of 2-methyl-1-acetyl cyclohexanols (I) and (II) are given in the table. It was ascertained that 2-methyl-1-acetyl cyclohexanol in the cis-configuration exists predominantly in the conformation "ae", whereas in the trans-configuration it exists in form of an "ee"-conformation. There are 2 figures, 1 table, and 5 references, 3 of which are Soviet.

ASSOCIATION: Institut goryuchikh iskopayemykh Akademii nauk SSSR  
(Institute of Mineral Fuels of the Academy of Sciences USSR)  
Institut organicheskoy khimii im.N.D.Zelinskogo Akademii nauk SSSR  
(Institute of Organic Chemistry imeni N.D.Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: April 8, 1958

Card 3/3

SOV79-28-6-6/63

AUTHORS: Nazarov, I. N. (Deceased), Kamernitskiy, A. V., Akhrem, A. A.

TITLE: The Most Simple Analogues of Cortic Steroids (Prosteyshiye analogi kortikosteroidov) I. The Stereochemistry of Cyano-hydrin-Acetylene Synthesis. Configuration of the 1-Cyano- and 1-Ethynyl-2-Methylcyclohexanol-1 (I. Stereokhimiya tsiangidrinovogo i setilenovogo sinteza. Konfiguratsiya 1-tsiano- i 1-etinil-2-metiltsiklogeksanolov-1)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1458-1469 (USSR)

ABSTRACT: In the condensation of 2-methylcyclohexanone (formula 1) with hydrogen cyanide and acetylene in any case two stereo-isomeric cyanohydrins (one crystalline and one liquid), (II, III) and acetylene alcohols of unknown structure (IV, V) (Ref 3) are formed. It was of interest to the authors to determine the spatial structure of these compounds as well as the stereochemical reaction course of the synthesis of cyanohydrin and acetylene in the series of substituted cyclo-hexanone, which hitherto had not been dealt with. The ob-vious synthesis of crystalline derivatives of cyanohydrins

Card 1/3

SOV/79-28-6-6/63

The Most Simple Analogues of Cortic Steroids. I. The Stereochemistry of  
Cyanohydrin-Acetylene Synthesis. Configuration of the 1-Cyano- and 1-  
-Ethynyl-2-Methylcyclohexanol-1

(II) and (III) by saponification to the oxy acids does not easily take place (Refs 2, 4, 5), the cyanohydrins decomposing under the regeneration of (I) when the conditions are more stringent (Ref 5). Vel'vart (Ref 6) described a saponification of the cyanohydrin mixture (II) and (III) (Ref 6) in acetic acid saturated with hydrogen chloride, which was improved by the authors. On this occasion the authors obtained from the crystalline cyanohydrin (II) a 2-methylcyclohexanol-1-carboxylic acid (VI) almost quantitatively, with a melting point at  $110 \dots 111^{\circ}$ , and from the liquid isomer (III) the same acid with the melting point at  $94-95^{\circ}$  (VII). In the oxidation of the crystalline 1-ethynyl-2-methylcyclohexanol (IV) permanganate the higher melting oxy acid (VI) was obtained as well, and in this oxidation from liquid 1-ethynyl-2-methylcyclohexanol (V) the low melting oxy acid was obtained. This way the authors proved the formation of two isomeric cyanohydrins of the 2-methylcyclohexanol (II) and (III) in the cyanohydrin synthesis as well as their configurative connection with the acetylene alcohols (IV) and

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SOV/79-28-6-6/63

The Most Simple Analogues of Cortic Steroids. I. The Stereochemistry of  
Cyanohydrin-Acetylene Synthesis. Configuration of the 1-Cyano- and 1-  
Ethynyl-2-Methylcyclohexanol-1

(V). Thus the stereochemistry of the binding reactions of  
hydrogen cyanide and acetylene to the 2-methylcyclohexanone  
was investigated and the configuration of the obtained  
1-cyano-2-methyl-cyclohexanols and their derivatives (oxy  
acids, ketenes etc.) was determined. There are 24 references,  
3 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR  
(Institute of Organic Chemistry, AS USSR)

SUBMITTED: July 18, 1957

1. Acetylenes---Synthesis

Card 3/3

AUTHORS: Nazarov, I. N., (Deceased),  
Akhrem, A. A.

SOV/79-28-7-16/64

TITLE: The Most Simple Analogs of Corticosteroids (Prosteyskiye analogi kortikosteroidov) II. The Introduction of the Dicarboxylic, Glycerin- and Oxyacetone Side Chain Into the o-Methyl Cyclohexanone, and the Stereochemistry of the Compounds Forming in This Reaction (II. Vvedeniye dioksidokarbonovoy, glitserinovoy i oksiatsetonovoy bokovykh tsepey v o-metiltsiklogeksanon i stereo-khimiya obrazuyushchikhsya pri etom soyedinenii)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 7,  
pp 1791 - 1805 (USSR)

ABSTRACT: The importance of the introduction of the dioxy acetone side chain into the cyclic compound which could lead to the complete synthesis of cortisone and of its homologs caused the authors already earlier (Ref 1) to deal with this problem. The introduction of the above mentioned side chains were tried with o-methyl cyclohexanone. It was shown for the first time that the intramolecular regrouping of the acetates of the cis- and trans-2-methyl-1-( $\omega$ -dibromoacetyl)-cyclohexane-1-ol does not

Card 1/3

The Most Simple Analogs of Corticosteroids. II. The Introduction of the Dicarboxylic, Glycerin- and Oxyacetone Side Chain Into the o-Methyl Cyclohexanone, and the Stereochemistry of the Compounds Forming in This Reaction

SOV/79-28-7-16/64

take place stereospecifically, and that on this occasion all four predicted racemic dioxy carboxylic acids form, viz: cis-2-methyl-1-oxy-cyclohexyl glycolic acids and trans-2-methyl-1-oxy-cyclohexyl glycolic acids. It was possible to convert the reduction of these acids into the corresponding triols, the cis-2-methyl-1-oxy-cyclohexyl glycol and the trans-2-methyl-1-oxy-cyclohexyl glycol. It showed that different from tertiary vinyl alcohols, the cis- and trans-vinyl-2-methyl-cyclohexane-1-ols, the oxidation of the acetates of these alcohols by means of preacetic acid takes an anomalous course, and that in the place of the expected glycolides two glycols are obtained (cis- and trans-2-methyl-1-acetoxycyclohexyl glycols). There are 11 references, 5 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry, AS USSR)

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SOV/79-28-7-16/64  
The Most Simple Analogs of Corticosteroids. II. The  
Introduction of the Dicarbon-, Glycerin- and Cxyacetone Side Chain into the  
o-Methyl Cyclohexanone, and the Stereochemistry of the Compounds Forming  
in This Reaction

SUBMITTED: July 18, 1957

1. Hexznones--Molecular structure    2. Cyclic compounds--Chemical  
reactions    3. Stereochemistry

Card 3/3

AUTHORS: Nazarov, I. N., (Deceased), Akhrem, A. A., SOV/79-28-7-17/64  
Kamernitskiy, A. V.

TITLE: Stereochemical Investigations in the Field of Cyclic Compounds  
(Issledovaniye v oblasti stereokhimii tsiklicheskikh soyedineniy)  
28. The Spatial Direction of the Serini Reaction in the Series  
of Cyclohexane (28.Prostranstvennaya napravlennost' reaktsii  
Serini v ryadu tsiklogeksana)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 7, PP 1805 - 1810  
(USSR)

ABSTRACT: The author realized for the first time the reaction of the  
cyclohexanone cyanohydride as well as of the cis- and trans-  
cyanohydrines of 2-methylcyclohexanone with magnesium methyl  
iodide with preceding protection of the hydroxyl group of the  
cyano-hydrines by vinyl-ethyl ether. The reaction of the cyano-  
hydrines with this ether was carried out in the presence of an  
ether solution of hydrogen chloride with the corresponding  
acetals (formula II) being obtained. On the action of magnesium  
methyl iodide on these acetals acetyl cyclohexanols (III) were  
obtained. The stereoisomeric hexanols (IV) and (VII) were re-  
duced by the aluminum isopropylate in toluene solution, with

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Stereochemical Investigations in the Field of Cyclic Compounds. 28. The Spatial Direction of the Serini Reaction in the Series of Cyclohexane SOV/79-28-7-17/64

only a hexanol (V) in crystal form being obtained from the cis-ketene (IV) and the liquid hexanol (VIII) from the trans-ketene (VII). The compounds (V) and (VIII) after partial acetylation lead to the monoacetates (VI) and (IX). These and other experiments showed that in the synthesis of the stereoisomeric 1-( $\alpha$ -oxyethyl)-2-methyl-cyclohexanols this reaction according to Serini in the cyclohexane series takes place stereospecifically, and that it leads to a change of the configuration. There are 14 references, 6 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry, AS USSR)

SUBMITTED: July 8, 1957

Card 2/3

Stereochemical Investigations in the Field of Cyclic      SOV/79-28-7-17/64  
Compounds. 28. The Spatial Direction of the Serini Reaction in the Series of  
Cyclohexane

1. Cyclic compounds--Chemical reactions
2. Cyclohexane--Chemical reactions
3. Stereochemistry

Card 3/3

AUTHORS: Nazarov, I. N. (Deceased), Aleksandrova, SOV/79-28-8-41/66  
G. V., Akhrem, A. A.

TITLE: The Simplest Analogs of the Corticosteroids (Prosteyskiye analogi kortikosteroidov) III. Introduction of the Dioxyacetone-, Glycerine- and Dioxypropanecarbon Side Chains Into the Derivatives of Cis- and Trans-Decalins (III. Vvedeniye dioksiatsetonovoy, glitserinovoy i dioksipropankarbonovoy bokovykh tsepey v proizvodnyye tsis-i trans-dekalinov)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 8, pp. 2187- 2198 (USSR)

ABSTRACT: Previously, the authors had described the synthesis of the trans-1-ethynyl-1-decalol (I) and (II), cis-1-ethynyl decalol (III) and their acetates (IV)-(VI). The present paper investigates the transformations of the cis- and trans-1-ethynyl decalols and their acetates in compounds which have an hydroxy acetone-, a glycerine- and a carbon-dioxypropane side chain. The dibromo ketol- and glycide method, elaborated by the authors, was applied (Ref 2). Besides, the stereochemistry of the products formed was investigated. Six stereoisomers of the trans- and cis-1-

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SOV/79-28-8-41/66  
 The Simplest Analogs of the Corticosteroids. III.  
 Introduction of the Dioxyacetone-, Glycerine- and Dioxypropanecarbon  
 Side Chains Into the Derivatives of Cis- and Trans-Decalins

hydroxy-decalyl glycol, four 1-hydroxy-decalyl ethylene  
 oxydi-isomers and five 1-hydroxy-decalyl glycolic acid isomers  
 of the transdecalin series were isolated. The previously  
 described (Ref 1) steric hindrance in the side chain in the  
 trans-1-ethynyl-1-decalol (II), in comparison with the  
 acetylene alcohol (I), which, for instance, occurs in the  
 hydration reactions, was amply verified by this study. This  
 becomes manifest in the more inhibited saponification of  
 the acetate of dibromo ketol (XII), in the incapability  
 of forming the acetonates of the dioxy acids (XIII) and  
 (XIV) and finally in the impossibility to realize the oxi-  
 dation of the hydroxyl group in the bromohydrine (XXXIX)  
 as well as the substitution of the bromine atom the former  
 by the hydroxyl- or acetoxy group. There are 7 references,  
 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute  
 of Organic Chemistry, AS USSR)

Card 2/3

The Simplest Analogs of the Corticosteroids. III. SOV/79-28-8-41/66  
Introduction of the Dioryacetone-, Glycerine- and Dioxypropanecarbon  
Side Chains Into the Derivatives of Cis- and Trans-Decalins

SUBMITTED: June 18, 1957

Card 3/3

AUTHORS: Nazarov, I. N., (Deceased), Aleksandrova, G.V., Akhrem, A. A. SOV/79-28-8-42/66

TITLE: Synthesis and Conversions of the Cis- and Trans-1-Ethynyl-1-Decalol (Sintez i prevrashcheniya tsis- i trans-1-etinil-1-dekalolov)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 8, pp. 2199 - 2207 (USSR)

ABSTRACT: The interest in the synthesis of the simplest analogs of the steroid hormones and, in particular, of the corticosteroids, is of a general nature. Many investigations are found (Refs 1-6) in the field of the cyclohexane-, dioxy-methyl cyclohexane-, cyclopentane-, perhydroindene- and decalin derivatives, which present evidence bearing on methods for the introduction of the dioxyacetone- and glycerine side-chains, being characteristic for the natural corticoid hormones. Compounds with a distinct corticoid activity were obtained (Refs 5,9, 10). Therefore, the authors tended to carry out the condensation of the cis- and trans- $\alpha$ -decalone with acetylene in order to utilize the formed acetylene alcohols for the introduction

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Synthesis and Conversions of the Cis- and Trans-1-Ethynyl-1-Decalol

SOV/79-28-8-42/66

of the oxidized side-chains into the nucleus of the decalin according to their own methods. The condensation of the trans- $\alpha$ -decalone (II) with acetylene occurred in the presence of pulverized caustic potash under pressure and also in a solution of liquid ammonia in the presence of sodium (Refs 12,13). In the latter case a mixture of isomeric trans-1-ethynyl-1-decalols was obtained in 90% yield from which by refrigeration at  $-70^{\circ}$  and chromatography of the residue on aluminium oxide the isomeric trans-1-ethynyl-1-decalols (II) and (III), in a ratio of 1 : 2, could be isolated. It is known that the cis- $\alpha$ -decalone is readily isomerized into the trans- $\alpha$ -decalone under the influence of acids and alkali liquors (Refs 14,15). Therefore, it was regarded as impossible to obtain, under highly alkaline conditions, the cis-1-ethynyl-1-decalols with the aid of acetylene according to A. S. Davanov. In the reaction of the cis- $\alpha$ -decalone (IV) with sodium acetylenide in liquid ammonia, however, the reaction of condensation with acetylene was predominant over the isomerisation. The cis-1-ethynyl-1-decalol (V) was obtained in a yield of 60%. Only 10% of the cis- $\alpha$ -decalone were

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Synthesis and Conversions of the Cis-and Trans-1-Ethynyl-1-Decalol

SOV/79-28-8-42/66

undergoing isomerization and were isolated as trans- $\alpha$ -decalone (I). Hydration products of the compounds (II), (III) and (V) were synthesized and some stereochemical reactions of these compounds were investigated. There are 1 figure and 22 references, 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry, AS USSR)

SUBMITTED: July 18, 1957

Card 3/3

NAZAROV, I.N. [deceased], akademik; ALEKSANDROVA, G.V.; AKHREM, A.A.

Synthesis and transformations of cis- and trans-1-ethynyl-1-decalols.  
Dokl. AN SSSR 119 no.708-711 Ap '58. (MIRA 11:6)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.  
(Naphthol) (Stereochemistry)

SOV/20-120-4-25/67

AUTHORS: Batuyev, M. I., ~~Akhram, A. A.~~, Matveyeva, A. D.,  
Kamernitskiy, A. V., Nazarov, I. N., Member, Academy of  
Sciences, USSR (Deceased)

TITLE: Optical Investigation of the Conformations of Some Gem-Sub-  
stituted Cyclohexanes (Opticheskoye issledovaniye konfor-  
matsiy nekotorykh gem-zameshchennykh tsiklogeksanov)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 4, pp. 779-782  
(USSR)

ABSTRACT: The physical properties and the reactivity of the functional  
group depend on its position and conformation. The position  
can be axial or equatorial. This can sometimes be determined  
chemically but frequently only by means of physical methods  
(Refs 1, 2). The authors deal with the optical determination  
of the conformation of epimeric 2-methyl-ethynyl cyclo-  
hexanols (I), (II), furthermore, with that of 1,2-dimethyl  
cyclohexanols (III), (IV) which they had already earlier  
synthesized (Ref 3); the method is described in short and a  
survey of publications is given (Refs 3, 4). Formerly the  
acetylene alcohols (I) and (II) were traced back by the

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SOV/20-120-4-25/67

Optical Investigation of the Conformations of Some Gem-Substituted Cyclohexanes

authors to the well known pair of cis- and trans-carbinols (III) and (IV) without touching the asymmetric center (Ref 3). The physical properties of the produced compounds (I) - (IV) are shown in table 1. The spectra of the combination light dispersion in the liquid phase were taken on the spectrogram ISP -51 of a mercury lamp having a chamber of the exciting blue line of 4358 Å. The numerical results of these measurements are given together with data on the intensity of the lines. Furthermore, spectra were taken of 10 % solutions of the first 2 substances in carbon tetrachloride. The presence of the 2 isomers I and II and of their solutions in CCl<sub>4</sub> in the spectra in the range of 3 - 4 (instead of only one)<sup>4</sup> characteristic frequencies of other weak lines (Table 2) tends to show, that other conformations are present in small numbers (possibly even in bath-tub shape) in the mixture where conformations prevail. The prevailing conformation in the cis-isomer (I) is "ae" (according to Ref 1) whereas in the trans-isomer it is "ee" (see scheme). In the ae-conformation the influence of the cycle on the hydroxyl group in the equatorial position is more intensive than in "ee", where it is in axial position. In the ae-conformation the

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SOV/20-120-4-25/67

Optical Investigation of the Conformations of Some Gem-Substituted Cyclohexanes

hydroxyl group is more protonized than the axial group in "ee". On the other hand the bindings  $\text{C}=\text{C}$ ,  $\text{C}-\text{C}$  in  $-\text{C}=\text{CH}$  in the equatorial position which they take in the "ee" conformation are more amply supplied with electrons. That means they have higher oscillation frequencies, binding energies and a shorter interatomic distance than they would have in an axial position in an "ae" conformation (Refs 1, 6). The interaction between reactivity and conformation in the series of cyclohexane derivatives was already at an earlier time observed by the authors. (Ref 7). Cis- $\alpha$ -ketole (V) which was obtained from an equatorial acidous hydroxyl can be acylated under milder conditions than trans- $\alpha$ -ketole (VI) which was produced from (II) with the hydroxyl being in an axial position. There are 2 tables and 7 references, 4 of which are Soviet.

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SOV/20-120-4-25/67

Optical Investigation of the Conformations of Some Gem-Substituted Cyclohexanes

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR  
(Institute of Organic Chemistry AS USSR).  
Institut goryuchikh iskoravemvkh Akademii nauk SSSR  
(Institute of Mineral Fuels AS USSR)

SUBMITTED: February 13, 1958

1. Cyclohexanes--Optical analysis    2. Cyclohexanes--Physical  
properties    3. Substitution reactions    4. Hydroxyl radicals  
---Chemical effects

Card 4/4

SOV/20-120-5-32/67

AUTHORS: Nazarov, I. H., Member, Academy of Sciences, USSR (Deceased),  
Akhrém, A. A.

TITLE: Introduction of Dioxycarbon, Glycerin, and Oxyacetone Side  
Chains Into Orthomethyl Cyclohexanone and the Stereochemistry  
of the Compounds Thus Formed (Vvedeniye dioksikarbonovoy,  
glitserinovoy i oksialsetonovoy bokovyykh tsopey v orto-me-  
tiltsiklogeksanon i stereekhiniz obrazuyushchikhsya pri  
etom soyedineniy)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 5, pp.1045-1048  
(USSR)

ABSTRACT: Recently (Ref 1) the authors described several methods of  
introducing oxidized side chains into the cyclic compounds  
using accessible acetylene alcohols and their derivatives.  
It is known that the introduction of a dioxy-acetone side  
chain is an important problem in the synthesis of cortico-  
steroids (among them cortisone with analogues). The authors  
were the first to find that the affiliation reaction of the  
hypobromous acid to the tertiary alcohols and their acetates  
takes an anomalous course in the case of the first and leads

Card 1/4

SOV/26-120-5-32/67

Introduction of Dioxycarbon, Glycerin, and Oxyacetone Side Chains Into Ortho-methyl Cyclohexanone and the Stereochemistry of the Compounds Thus Formed

to the formation of unsaturated dibromides instead of the expected bromo ketoles. In the present paper the results of the introduction of an oxidized side chain into the substance (I) mentioned in the title are described in short. In consequence of a condensation of the ketone I with acetylene under pressure (Ref 2) in the presence of powdery caustic potash 2-methyl-1-ethyl-1-cyclohexanol is obtained with a high yield in the form of two epimers: a) crystalline (II) with a melting point of 56-57° and b) liquid (III) (melts at 75°/15 mm). Their ratio is 3:2 and depends apparently on the conditions of synthesis (Ref 3). The authors proved already previously (Ref 4) that (II) has a cis-configuration, whereas (III) represents its trans isomer. The author acetylated the alcohols II and III, and obtained the cis-acetate IV. Furthermore they caused hypobromous acid to act upon the latter. Crystalline acetate of the cis-1-( $\omega$ -dibromacetyl)-2-methylcyclohexanol (VI) was produced. After they had tested the action of other reagents the authors drew the conclusion that the oxidation of acetates of the tertiary vinyl alcohols by means of peracetic acid proceeds differently to that of

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SOV/20-120-5-32/67

## Introduction of Dioxycarbon, Glycerin, and Oxycetone Side Chains Into Ortho-methyl Cyclohexanone and the Stereochemistry of the Compounds Thus Formed

the acetates of corresponding vinyl alcohols and allyl alcohol acetates and does not lead to the formation of normal oxidation products (glycidic alcohol acetates, Ref 1). An analysis of configuration (Ref 5) makes possible to find a connection between the stereochemistry of a molecule and its reactivity. In connection with the hydration of the cis-alcohol II in a methanol solution in presence of mercury sulfate and sulfuric acid cis- $\alpha$ -ketole XXXIV is produced with a melting point of  $37 - 38^{\circ}$  (Ref 6) in an almost quantitative yield. The authors conclude from the results that the tertiary hydroxyl in the cis- $\alpha$ -ketole XXXIV has an apparently equatorial configuration, whereas it has an axial position in the trans- $\alpha$ -ketole (Ref 7). This is confirmed by the investigation of the combination dispersion spectra (Ref 8). There are 8 references, 7 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. S. Zelinskogo Akademii nauk SSSR  
Card 3/4

001/20-120-5-32/67

Introduction of Dioxycarbon, Glycerin, and Oxycetone Side Chains Into Ortho-methyl Cyclohexanone and the Stereochemistry of the Compounds Thus Formed

(Institute of Organic Chemistry named N. D. Zelinskiy,  
AS USSR)

SUBMITTED: December 21, 1957

1. Cyclic compounds--Synthesis      2. Cyclic compounds--Molecular  
structure      3. Stereochemistry      4. Steroids--Synthesis

Card 4/4

AKHREM, A. A.: Doc Chem Sci (diss) -- "Investigation of the synthesis and stereochemistry of analogues of the corticosteroids. Methods of building and the stereochemistry of the corticoid side chain". Moscow, 1959, published by the Acad Sci USSR. 30 pp (Acad Sci USSR, Inst of Organic Chem in N. D. Zelinskiy), 200 copies (KL, No 11, 1959, 115)

5(4)

AUTHORS:

Batuyev, M. I., Akhrem, A. A.,  
Kamernitskiy, A. V., Matveyeva, A. D.

SOV/62-59-3-31/37

TITLE:

Optical Investigation of the Conformations of the Cis- and Trans-methyl Esters of 3-Methyl Cyclohexanol Carboxylic Acids (Opticheskoye issledovaniye konformatsiy tsis- i trans-metilovykh efirov 3-metiltsiklogeksanolkarbonovykh kislot)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 3, pp 556-558 (USSR)

ABSTRACT:

This is a brief communication on the investigation of the cis- and trans-methyl esters of 3-methyl cyclohexanol carboxylic acids which were synthesized according to the scheme described in reference 1. The physical properties of the products obtained are given in the table. It is known that the Auers-Skit formula for the cis- and trans-configurations of 1,3-disubstituted cyclohexanes may be applied in the reversible form. The same holds also for the esters investigated: the cis-compound has a lower density and a smaller refraction index than the trans-compound. The Raman spectra of the esters were recorded in the liquid phase by means of the ISP-51 spectrograph with a medium camera of the exciting line 4358 of the

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Optical Investigation of the Conformations of the SOV/62-59-3-31/37  
Cis- and Trans-methyl Esters of 3-Methyl Cyclohexanol Carboxylic Acids

quartz lamp. The cis- and trans-methyl esters of 3-methyl cyclohexanol carboxylic acids investigated are mixtures of reversible isomers  $1e3e \rightleftharpoons 1a3a$  and  $1e3a \rightleftharpoons 1a3e$ . In the second conformation  $1e3a$  mainly the first  $1e3e$  is present. Moreover, in each of these mixtures admixtures of one conformation are contained in the other. There are 1 table and 3 references, 1 of which is Soviet.

ASSOCIATION: Institut goryuchikh iskopayemykh Akademii nauk SSSR (Institute of Mineral Fuel of the Academy of Sciences, USSR). Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: July 30, 1958

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AU)  
AUTHOR:

Akhrem, A. A.

TITLE:

Symposium on Concepts of Conformation in Organic Chemistry  
(Soveshchaniye po konformatsionnym predstavleniyam v organicheskoy khimii )

SOV/62-59-3-35/37

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 3, 561-564 (USSR)

ABSTRACT:

This is a report on the symposium on concepts of conformation in organic chemistry which took place in Moscow at the IOKh AN SSSR (Institute of Organic Chemistry, AS USSR) from September 30 to October 2, 1958. This conference was convened by the Institute of Organic Chemistry imeni N. D. Zelinskiy AS USSR and the Councils of Scientists for problems of the "Theory of the Chemical Structure, Kinetics and Reactivity" and the "Synthesis and Investigation of Natural Biologically Important Compounds". In his opening speech Academician B. A. Kazanskiy emphasized the importance of the concepts of conformation in stereochemistry. He pointed out that the purpose of this symposium was to determine the present stage of investigations in this field. Moreover, the attention of Soviet scientists was drawn to the problems of stereochemistry.

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## Symposium on Concepts of Conformation in Organic Chemistry

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and conformation analysis since work in this field has not yet been sufficiently developed in the USSR. A. I. Kitaygorodskiy (INEOS AS USSR, Moscow) then delivered a lecture on the "Conformation of Organic Molecules and Methods for the Estimation of Their Degree of Stretching". A. L. Liberman (IOKh AS USSR) spoke on behalf of B. A. Kazanskiy and on his own behalf "On the Connection Between the Configurations of Dialkyl Cyclanes and Their Physical Properties". L. D. Bergel' - son (IOKh AS USSR, Moscow) spoke on behalf of L. P. Badenkova and on his own behalf on "Conformation of Acyclic Stereoisomers and Their Behavior During the SN2 Reactions". M. V. Vol'kenshteyn (IVS AS USSR, Leningrad) delivered a lecture on "Interior Rotation and Rotational Isomerization in Small and Big Molecules". O. B. Ptitsyn (IVS AS USSR, Leningrad) spoke on behalf of G. M. Birshhteyn, Yu. A. Sharonov and on his own behalf on "Interior Rotational Isomerism in Polyisobutylene and Polystyrene". The lecture of Yu. A. Pentin (Moscow) was entitled "Investigation of the Rotational Isomerism of Hydrocarbon Halogen Derivatives by Spectroscopic Methods". S. L. Mayants (INEOS AS USSR, Moscow) spoke "On Some Methods of Applying

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the Theory of Characteristic Frequencies for the Investigation of Conformations". M. M. Sushchinskiy (FIAN AS USSR, Moscow) spoke on "Investigation of the Rotational Isomerism of Paraffins by Means of the Raman Spectra". V. M. Tatevskiy (MGU, Moscow) spoke on behalf of Yu. A. Pentin, Ye. G. Treshchova, Kh. Kesler, and on his own behalf on "Rotational Isomerism and the Energy of the Formation of Hydrocarbons". In his second lecture Yu. A. Pentin dealt with the connection between the phenomenon of crystallization of organic compounds and the rotational isomerism. E. A. Mistryukov (IOKh AS USSR, Moscow) spoke on behalf of N. I. Shvetsov and on his own behalf on "Application of Concepts of Conformation for Determining the Conformation of Isomeric 1,2,3- and 1,2,5-Trimethyl-4-phenyl Piperidoles". On behalf of G. S. Litvinenko, K. I. Khludneva, and on his own behalf D. V. Sokolov (Institut khimii AN KazSSR, Alma-Ata)(Institute of Chemistry AS Kazakhskaya SSR, Alma-Ata) spoke on "Conformation of Stereoisomers of 2-Methyl-4-ketodekahydroquinoline and 2-Methyl-4-oxydekahydroquinoline and Some of Their Derivatives". Three further lectures dealt with the application of the rules of conformational analysis

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for the determination of the configuration of adducts of the diene synthesis. V. F. Kuchеров (IOKh AS USSR, Moscow) spoke on behalf of N. Ya. Grigor'yeva and on his own behalf on "Application of the Principles of Conformational Analysis for Proving the Configuration of Isomers of 3-Acetoxy Cyclohexane-1,2-dicarboxylic Acids". On behalf of V. F. Kuchеров and on his own behalf V. M. Andreyev spoke on the "Synthesis and Configuration of All Possible Isomers of 3,4-Dimethyl- $\Delta^4$ -cyclohexene- and 3,4-Dimethyl Cyclohexane-1,2-dicarboxylic Acids". On behalf of V. F. Kuchеров and on his own behalf G. M. Segal' spoke on the "Stereochemistry of the Oxidation of  $\Delta^4$ -Octaline Carboxylic Acids". A. A. Akhrem (IOKh AS USSR, Moscow) delivered a lecture on behalf of A. V. Kamernitskiy, G. V. Aleksandrova, I. N. Nazarov (deceased), and on his own behalf on the "Stereochemistry of Some Addition Reactions in Multiple Bonds". A. I. Kitaygorodskiy spoke on behalf of Yu. T. Struchkov on the "Conformations of Molecules of Sterically Stretched Benzene Polyderivatives". The symposium took

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place under active participation of the persons present. Some conferences were attended by up to 300 persons. The lecturers were asked numerous questions. Altogether 17 lectures were heard (21 lectures had been submitted). Many lectures were followed by lively discussions. The concepts of conformation and conformational analysis were the objects of especially heated discussions in which the opinions widely differed. Numerous discussants, chiefly physicists, were against these new expressions and they were of the opinion that the known concept of configuration and the concept of rotational isomer introduced by I. V. Obreimov in 1942 are sufficient. Their opponents, mainly chemists, were in favor of the introduction of the new concept. They were of the opinion that this concept has a much wider sense than the concepts of configuration and the rotational isomer. B. A. Kazanskiy, S. N. Danilov, V. M. Tatevskiy, M. V. Vol'kenshteyn, A. I. Kitaygorodskiy, A. L. Liberman, L. D. Bergel'son, M. G. Gonikberg, V. F. Kucherov, A. A. Akhrem, et al. took part in the discussions. It was recommended to the discussants to publish their opinions

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on this problem in chemical periodicals. More than 50 scientists took part in the discussion of the lectures delivered.

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5(3)

AUTHORS:

Kamernitskiy, A. V., Akhrem, A. A.

SOV/62-59-4-30/42

TITLE:

Effect of the Medium on the Stereochemistry of the Reactions of Nucleophilic Addition to the Carbonyl Group (Vliyaniye sredy na stereokhimiya reaktsiy nukleofil'nogo prisoyedineniya k karbonil'noy gruppe)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 740-742 (USSR)

ABSTRACT:

This is a brief report on the investigation of the cyanohydride synthesis. In addition to the cyanohydride synthesis by recyanization already described (Refs 1-3), the interaction of ketone (III) with potassium cyanide and hydrochloric acid in aqueous methanol and with anhydrous hydrogen cyanide in the presence of potash in absolute ether was investigated. Thus the cyanohydrine synthesis was carried out in ionogenic media (methanol, acetone, water) as well as in non-ionogenic media. The mixtures of cyanohydride (I) and (II) obtained were saponified with hydrochloric and acetic acid in the mixture of cis- and trans-oxy acids (VIII) and (IX) under similar conditions. The latter were methylated by means of diisomethine. The table shows the effect of the reaction conditions on

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Effect of the Medium on the Stereochemistry of the SOV/62-59-4-30/42  
Reactions of Nucleophilic Addition to the Carbonyl Group

the steric tendency of the cyanohydride synthesis with 2-methylcyclohexanone. The steric selectivity of the cyanohydrine synthesis is approximately similar in the first and second case (ionogenic conditions) and becomes slightly weaker under non-ionogenic conditions at the same time approaching the tendency of the acetylene synthesis. However, in this case, too, the formation of the cis-isomer dominates in contrast to the Grignard reaction. There are 1 table and 4 references, 3 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: July 31, 1958

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5(3)

AUTHORS:

Akhrem, A. A., Kamernitskiy, A. V.

SOV/62-59-4-34/42

TITLE:

Stereochemistry of the Reactions of the Nucleophilic Addition to the Carbonyl Group of 3-Methylcyclohexanone (Stereokhimiya reaktsii nukleofil'nogo prisoyedineniya po karbonil'noy gruppe 3-metiltsiklogeksanona)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 748-750 (USSR)

ABSTRACT:

In the investigation of the stereochemistry of the addition of hydrocyanic acid, acetylene, and methyl magnesium iodide to 2-methyl-cyclohexanone (I) a certain, although varying steric selectivity was found (Refs 1-3). In order to find out whether the discovered peculiarities of the steric tendency remain valid also with other examples the stereochemistry of the cyanohydrine synthesis and Grignard reaction was investigated in this work on 3-methylcyclohexanone (II) as an example. The cyanohydrine synthesis carried out on the basis of 3-methylcyclohexanone by means of acetone cyanohydrine (Ref 1) yielded a liquid mixture of 3-methylcyclohexanone-(VIII)-cyanohydrine. By saponifying this mixture a mixture of trans- and cis-3-methylcyclohexanol carboxyl-1-acids (IX)

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Stereochemistry of the Reactions of the Nucleophilic  
Addition to the Carbonyl Group of 3-Methylcyclohexanone SOV/62-59-4-34/42

and (X) was obtained. This mixture contains about 75 % trans-oxyacid (IX) and 25 % cis-oxyacid (X). The configuration of the oxyacids (IX) and (X) was proved by their reduction to 1,3-dimethylcyclohexanols (III) and (IV) without touching the asymmetrical centers. A mixture of alcohols (III) and (IV) was obtained from the reaction of the ketone (II) with methyl magnesium iodide. This mixture consists of 40 % trans-alcohol (III) and 60 % cis-alcohol (IV). It was found that the steric tendency of the cyanohydrine synthesis and Grignard reaction is similar to that appearing in the case of 2-methylcyclohexanone. There are 1 table and 13 references, 8 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: August 8, 1958

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5(3)

AUTHOR:

Akhrem, A. A.

TITLE:

Oxidation of 2-Methyl-1-(1'-acetoxy-ethylidene)-cyclohexane by Osmium Tetroxide and Peracetic Acid (Okisleniye 2-metil-1-(1'-atsetoksietiliden)-tsiklogeksana chetyrekhokis'yu osmiya i peruksusnoy kislotoy)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 750-752 (USSR)

ABSTRACT:

In the present work cis-2-methyl-1-(1',2'-dioxyethyl)-cyclohexanol (I) described earlier (Ref 1) was synthesized by oxidation of 2-methyl-1-(1'-acetoxyethylidene)-cyclohexane (II) with the anhydride of osmic acid. By the effect of osmic acid on acetate (II) in ether and subsequent boiling of the reaction product with an aqueous alcohol solution of sodium sulfite, triol was obtained as main product with a melting point of 90-90.5°. This obviously has "cis-treo" configuration. In addition to the well-known cis-triol (IV) a small quantity of the substance (V) with a melting point of 93-94° was precipitated out in the same experiment. It seems that this compound may either be one of the polymorphous forms of triol (IV) or a molecular compound of two epimeric triols

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